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Preparation of carbon-based transparent and conductive thin films by pyrolysis of silylated graphite oxides

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ABSTRACT

Thin films of silylated graphite oxide were obtained from a chloroform/cyclohexane dispersion of n-hexadecylamine-intercalated silylated graphite oxide by a casting method at a low temperature. Carbon-based thin films were obtained from the pyrolysis of the resulting films under a reduced pressure at 500 °C or higher temperatures. The resulting samples were well adhered to the substrate because of the presence of silicon containing species as a "glue". The resistivity decreased with an increase in the film thickness or a decrease in the transparency. Based on the data obtained for the samples prepared from graphite with different particle sizes and graphite oxide with different oxygen contents, the conduction of the electrons within each carbon sheet seemed important for large film thickness and conduction through the boundary seemed important when the film thickness was small. A low sheet resistance of 3.7 kΩ/sq for 80% of transmittance was achieved, when graphite oxide with a lower oxygen content was prepared from graphite with smaller particle sizes and the precursor film was heated at 500 °C. At 900 °C, it further decreased to a value of 700 Ω/sq.

1. Introduction

Transparent and conductive thin film electrode is widely used for liquid crystal display, solar cells, etc., and indium tin oxide (ITO)-coated glass is usually used. However, indium is not abundantly produced and expensive metal. In addition, it is conventionally fabricated by expensive and complex methods such as sputtering, chemical vapor deposition and so on. Therefore, recently, inexpensive and abundant carbon-based thin films prepared from graphite oxide (GO) are attracted much attention. Graphite oxide can be easily exfoliated to individual layers in an aqueous solution and restacking of them provides thin films. Chemical or thermal reduction of the resulting thin films can provide transparent and conducting thin films and many reports on it have been provided together with those on the electrical properties of reduced graphite oxide monolayers [1–11]. Chemical reduction of GO by, for example, hydrazine monohydrate greatly changes the electronic properties of it from insulator to semi-metal [12], but the conductivity of the resulting films is so not high. In order to obtain the film with higher conductivity, thermal treatment of GO is needed and it reached 1 kΩ/sq. for the film with 80% of transparency at 550 nm when the precursor film was heated at 1100 °C [9]. However, it seems that the adhesion to the substrates is poor because there is no strong interaction between carbons and them. Here, in this study, we introduce the preparation of transparent and conducting carbon-based thin films from the dispersion of

n-hexadecylamine-intercalated silylated graphite oxide in an organic solvent. It is expected that the silicon containing groups attached to graphite oxide act as "glue" after thermal reduction of it. In addition, recent researches have shown that various types of defects in the graphene plane limit the transport of electrons in reduced GO films [12] and the band structure of GO can be tailored by changing the oxidation times of the starting graphite [13]. These suggest that the properties of GO used as the precursor can change the conductivity of the resulting films. In case of the film with the large area, the conduction of electrons through the boundary between the reduced GO sheets also seems important in order to obtain the film with higher conductivity. Therefore, in this study, the effects of particle size of the starting graphite and the degree of oxidation of it on the properties of carbon-based thin films were also investigated.

2.   Experimental

GO was prepared by oxidizing graphite powders with different particle sizes of 1–2 μm (synthetic, Aldrich) and 57–74 μm (natural graphite) with $KClO_3$ in fuming nitric acid at 60 °C for 3 h, based on the Brodie's method [14]. This oxidation procedure was repeated for five times when the larger graphite was oxidized. The compositions of the obtained GO samples determined based on the elemental analysis data of carbon and hydrogen were summarized in Table 1, together with their interlayer spacings. The letters "L" and "S" mean the large and smaller graphite powder and the numbers of "1" and "5" mean the times of oxidation procedure repeated.

The contents of oxygen and hydrogen in GO-L-5 were slightly larger than those in GO-S-1, though the particle size of the pristine graphite was lager. In this study, GO-L-5 was firstly used because the silylated sample seemed relatively well dispersed in organic solutions when n-hexadecylamine was added. Hereafter, it was used as a starting material for the carbon films, if not specified. GO (100 mg) was silylated with octyltrichlorosilane ($C_8H_{17}SiCl_3$, hereafter abbreviated as C_8Si; 2.0 ml) in the presence of n-butylamine ($C_4H_9NH_2$ hereafter abbreviated as C_4; 2.0 ml) under an argon atmosphere for 1 day at 60 °C [15,16]. After centrifugation, the precipitate was washed with acetone several times. The obtained samples were dried at 60 °C under reduced pressure for 12 h. The contents of silylating reagent per GO unit were 0.66 and 0.55 for GO-L-5 and GO-S-1, respectively, based on the Si content calculated from the weight of residual SiO_2 after thermogravimetric measurement and assuming that the sample contained 0.4 residual C_4 molecules per GO unit. In order to disperse the obtained silylated GO in organic solvents, n-hexadecylamine ($C_{16}H_{33}NH_2$ hereafter abbreviated as C_{16}) was intercalated into C_8SiGO as previously reported [17,18]. In the presence of a small amount of hexane ca 0.5 ml, C_8SiGO

and C_{16} with weight ratio of 1 were well mixed in a pestle until hexane molecules evaporated. The obtained sample was dispersed in a chloroform/cyclohexane solution (0.05–10 mg/ml, 1:1 by volume) and sonicated, resulting in the light to dark brown homogenous and stable dispersion. The dispersion was cast on a glass or quartz substrate (0.05 ml/cm²) and the solvent was allowed to evaporate slowly by putting a glass vial of 110 ml on it at 2 °C. The resulting thin film was immersed in ethanol for 30 min and C_{16} was removed. Then, it was pyrolyzed under vacuum for 1 h between 500 and 900 °C. The temperature increasing rate was 1 °C/min. For comparison, carbon film without silicon containing species was prepared from C_{16}-intercalated GO [18] in a similar manner. The products were analyzed X-ray diffraction, UV–Vis spectroscopy, ellipsometry (Otsuka Denshi FE5000) and Raman spectroscopy (Horiba–Jovin Yvon T-64000, excitation wavelength: 514.5 nm). The adhesion strength was evaluated by the scotch tape test. The tape was pressed onto the film (20 × 20 mm) until the film was well visible and then it was peeled off within about 1 s. The absorption spectra of the resulting films were measured. Electrical conductivity was measured by four probe method by applying alternating current using Hioki 3532-8 chemical impedance meter or by the potential sweep method using a potentiostat (Hokuto Denko SV-100) at a sweep rate of 1 mV/s between −1 and 1 V. The morphology of the C_8SiGO particles was observed by atomic force microscopy (AFM, Digital Instruments Nanopics1000).

3.   Results and discussion

3.1.   Preparation of carbon-based thin film from silylated GO

Fig. 1 shows the X-ray diffraction patterns of C_{16}–C_8SiGO films before and after washing with ethanol and after heated at 500 °C, together with those of GO-L-5 and C_8SiGO powder samples. The diffraction peak at $2\theta = 11.78°$ ($d = 0.75$ nm) observed for the pristine GO shifted to a lower angle of $2\theta = 5.66°$ ($d = 1.56$ nm) after silylation. This peak further shifted to $2\theta = 2.74°$ ($d = 3.22$ nm), when C_{16} was added to the C_8SiGO powder, which shows that the C_{16} molecules were intercalated into C_8SiGO. The peak position was unchanged for the C_{16}–C_8SiGO film and it shifted to a higher angle of $2\theta = 5.58°$ ($d = 1.58$ nm) after washed with ethanol. This value was almost the same as that observed for C_8SiGO powder, indicating that most of the C_{16} molecules were de-intercalated from C_8SiGO, though the diffraction peak became somewhat broader. When the C_8SiGO film was heated at 500 °C, a very broad peak centered at $2\theta = 25.5°$ ($d = 0.349$ nm) appeared, indicating that the silylated GO decomposed to carbon. As shown in our previous paper, thermal decomposition of silylated GO with long alkyl chain provides silica–carbon

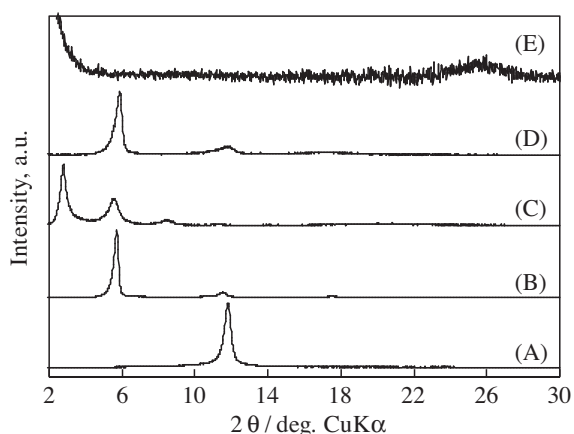| Table 1 – Composition and interlayer spacing of graphite oxides used in this study.					
Sample	C (%)	H (%)	O (%)	Composition	Ic (nm)
GO-L-5	52.15	1.73	46.13	C8O5.3H3.2	0.75
GO-S-1	55.02	1.68	43.30	C8O4.7H2.9	0.70

Fig. 1 – X-ray powder diffraction patterns of (A) GO, (B) C$_8$SiGO, C$_{16}$–C$_8$SiGO thin film (C) before and (D) after washing with ethanol, and (E) carbon thin film obtained from the pyrolysis of C$_8$SiGO thin film at 500 °C.

composites when the content of silylating reagent was low [19,20]. In this case, silylating reagents bound to GO layers were removed, providing carbon and most likely silica.

Fig. 2 shows the UV–Vis spectra of C$_8$SiGO film before and after heating at 500 °C. Two peaks appeared at 222 and 298 nm for C$_8$SiGO film, which are typically observed for GO [7,10,21]. This indicates that the electronic structure of GO was not affected by silylation or intercalation of C$_{16}$. After heating, the peak at 298 nm disappeared and a peak at 263 nm was observed. At the same time, the absorbance in the region of visible light greatly increased. This is consistent with the previous reports [7,22] and carbon film was successfully reduced, though the silicon containing species should co-exist. Fig. 3 shows the UV–Vis spectra of carbon films prepared on glass substrate before and after tape test. These spectra were almost identical and the carbon-based film was well adhesive to the glass substrate. Since the absorbance of the carbon film prepared from C$_{16}$-intercalated GO without silylating reagent greatly decreased after tape test, it is reasonable to think that the silicon containing species formed as the result of the decomposition of silylated GO worked as a "glue".
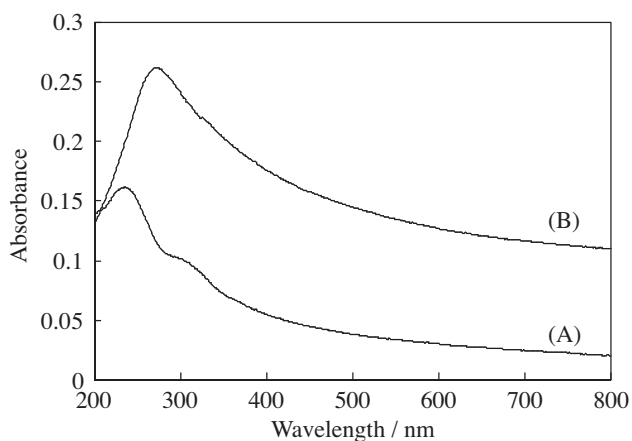

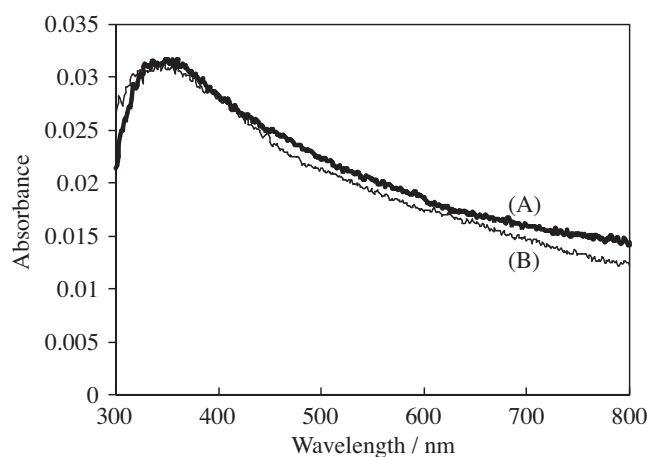**Fig. 2 – Absorption spectra of C$_8$SiGO thin film (A) before and (B) after pyrolysis at 500 °C.**

Fig. 3 – Absorption spectra of carbon prepared from the pyrolysis of C$_8$SiGO thin film on glass substrate (A) before and (B) after tape test.

3.2. Film thickness

Fig. 4 shows the relationship between the wavelength and absorption of the sample prepare from the dispersion of 0.20 mg/ml measured at the incident angles of 60°, 65° and 70° under air. Here, the data of tanψ and cosΔ was fitted using a three-phase model (quartz, carbon and air) in a similar manner to that reported previously [23]. The back side reflection correction was performed, since the present samples on quartz were transparent. For the optical constants of refraction index and values for carbon layers, polynominal function was used. This is because the present samples contained not only carbon but also silicon containing species and as shown later, the substrate was not densely covered with the carbon film. Fig. 5 shows the ellipsometric data of tanψ and cosΔ as a function of the wavelength, together with the fitted curves. Based on these results, the thickness of this film was determined to be 25.1 nm.

Fig. 6 shows the relationship between the absorbance at 400 nm and the thickness calculated based on the data of ellipsometry. The absorbance almost linearly increased with the increase in the thickness with the slope of 0.0032 nm^{-1}. This slope was much smaller than those reported previously [5], probably because the density of the film was low as
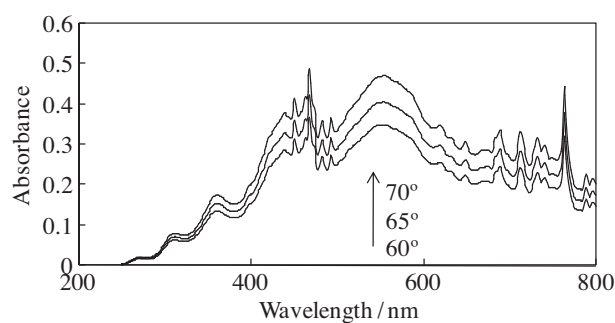

Fig. 4 – Variation of absorbance at various incident angles as a function of wavelength for the carbon film prepared from the dispersion of 0.2 mg/ml.
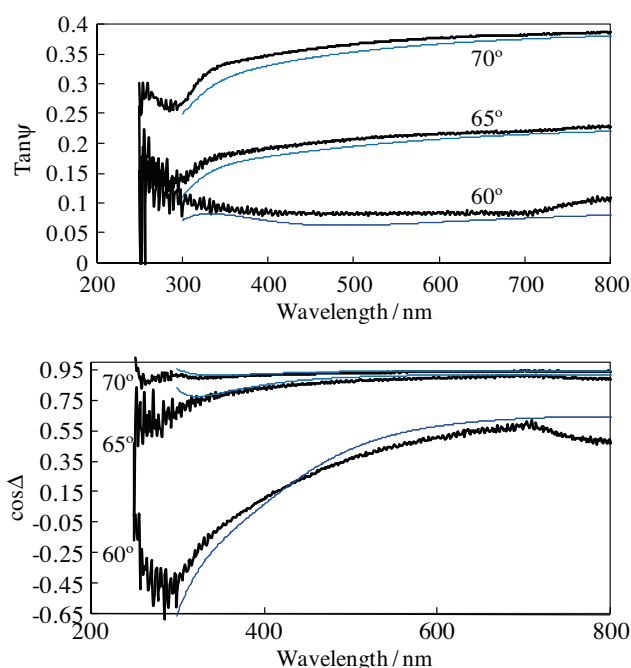
Fig. 5 – Ellipsometry data of tanΨ and cosΔ for the carbon film prepared from the dispersion of 0.2 mg/ml, together with the fitted curves (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
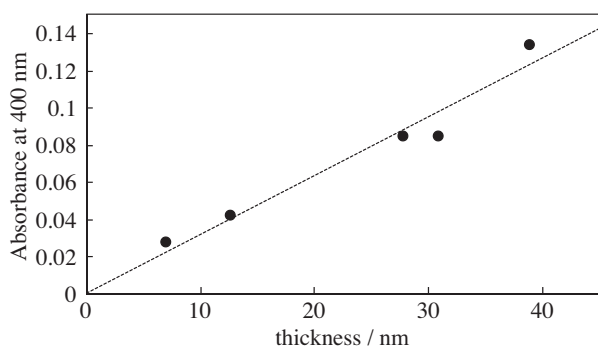

Fig. 6 – Relationship between the absorbance of the carbon films at 400 nm and the thickness of them estimated from ellipsometry data.

suggested from the data of ellipsometry. Silica particles formed as the result of aggregation of the de-intercalated silicon containing species from GO layers would prevent the dense packing of the carbon layers. Based on the visual transparency of graphene of 97.7% [24], the number of carbon layers should be much less. This means that the transparency of the carbon from silylated GO was higher than that of graphene.

3.3. Conductivity of carbon-based thin films

Fig. 7 shows the relationship between the resistivity of the film prepared from C_8SiGO-L-5 and the transparency of it for the films prepared at various temperatures. As was observed

in the previous studies [5,6], it decreased with the decrease in the transmittance of the films and became almost constant values for the thicker films. These values are very similar to or lower than those reported for the carbon films prepared from aqueous suspension of GO [1–11]. The conduction between the adjacent carbon layers seems important when the thickness of the film becomes smaller. For thicker films, this boundary effect becomes less important and the resistivity of the film would approach to that of individual carbon sheets. When the temperature for pyrolysis increased the sheet resistance reached a very low sheet resistance of 700 Ω/sq at 80% of transmittance for the film obtained at 900 °C.

Fig. 8 shows the Raman spectra of the carbon-based films prepared at 500 and 900 °C. In both spectra, two broad peaks at around 1360 and 1600 cm^{-1} were observed, which are ascribed to D and G bands, respectively. The latter slightly shifted from 1600 cm^{-1} to lower wavenumber of 1595 cm^{-1}, when the heat treatment temperature increased. At the same time, the relative intensity of G band to D band decreased. This peak ratio reflecting the graphitization degree usually increases with the increase in the heat treatment temperature. In the present case, the number of defects in the carbon layers is expected to increase when the heat treatment temperature increases, because the removal of oxygen containing groups from the layers of GO could be accompanied by that of the carbon atoms within the layers. This was commonly observed when GO powder without silylating reagent was pyrolyzed under hydrogen gas flow as reported in our previous study [25]. When the temperature became higher, the interlayer spacing slightly decreased from 0.347 and reached the value of 0.336 nm which was very similar to that of the graphite, though the diffraction peak was very broad. This decrease in the interlayer spacing was also observed when GO without silylating reagent was heated under reduced pressures or reducing atmospheres [25–28]. At the same time, the G band in the Raman spectrum in Fig. 8 became somewhat sharper. These indicate the increasing graphitic struc-
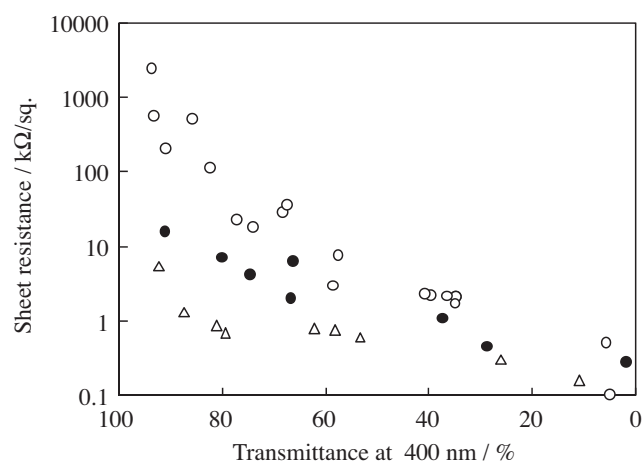

Fig. 7 – Variation of the sheet resistance of carbon films prepared from GO-L-5 at various temperatures of (○), 500; (●), 700 and (△), 900 °C as a function of their transmittance.
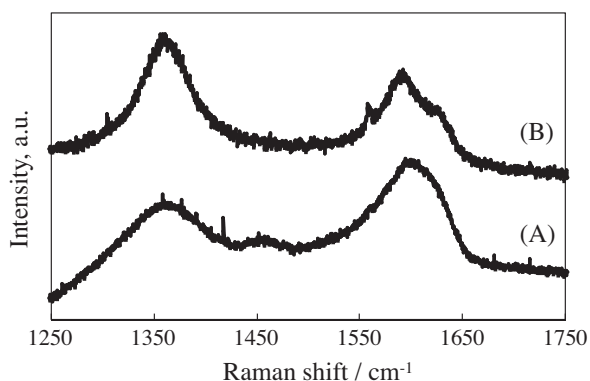
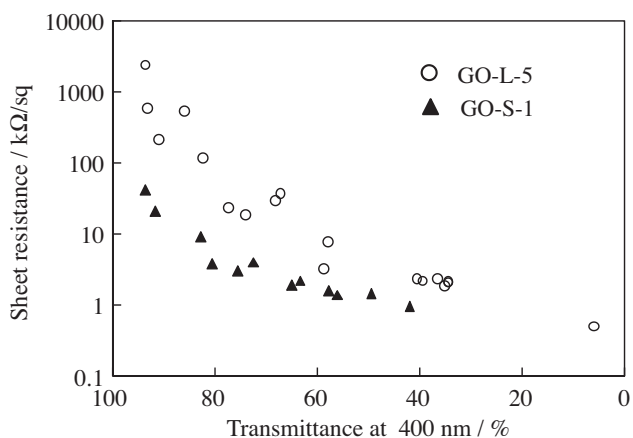**Fig. 8 – Raman spectra of carbon films prepared at (A) 500 and (B) 900 °C.**

Fig. 9 – Variation of the sheet resistance of carbon films prepared from (○), GO-L-5 and (▲), GO-S-1 as a function of their transmittance.

the electrical conductivity increased as the increase in the heat treatment temperature.

Fig. 9 shows the sheet resistance of the carbon-based thin film prepared from GO-S-1, together with those of the film from GO-L-5 shown in Fig. 7. It was almost 10 times lower, especially when the transmittance of the film was higher for the films from GO-S-1. For the films with lower transmittance, the sheet resistance of the carbon films from both GO-S-1 and GO-L-5 became similar. The lowest resistance of 3.7 kΩ/sq for 80% of transmittance was achieved for the film obtained from GO-S-1.

Fig. 10 shows the AFM images of the C_8SiGO films obtained from GO-L-5 and GO-S-1, which were deposited on a mica surface. The height of the C_8SiGO sheets on mica was 2.0–3.7 nm, based on the line profiles of them. Considering the thickness of GO-L-5 (about 0.7 nm) and the interlayer spacing of the C_8SiGO (about 1.6 nm), the thickness of silylating reagents on GO is calculated to be 0.9 nm. The silylating reagents are bonded to both sides of the GO layers, therefore, the thickness of the C_8SiGO monolayer is the sum of the thickness of GO and twice of that of the silylating reagents. The value of 2.5 $(0.7 + 0.9 \times 2)$ nm is obtained and this is similar to those observed above, indicating that the C_8SiGO monolayers were observed in these images. The lateral sizes of the monolayers of C_8SiGO obtained from GO-L-5 were 100–400 nm. On the other hand, several larger platelets with the sizes of 400–1000 nm were also observed for C_8SiGO from GO-S-1, together with the smaller particles with the sizes of 50–300 nm. As was expected from the higher contents of oxygen and hydrogen in GO-L-5, the carbon sheets were more severely damaged because the pristine graphite was oxidized repeatedly. This can lead to the decrease of the lateral sizes of the carbon sheets. Larger particles probably can contact more easily with each other when the film was formed and the numbers of boundary of particles are smaller. These can reduce the resistivity of the boundary of the platelets, which well explains the lower sheet resistance of the carbon films from GO-S-1 especially in the region of the higher transmittance. The effect of the silicon content was also investigated using C_8SiGO samples with various contents of silylating reagent between 0.2

ture most likely because of the removal of oxygen atoms bonded to carbon layers. In the present case, the latter effect of increasing graphitic structures was dominant, therefore,
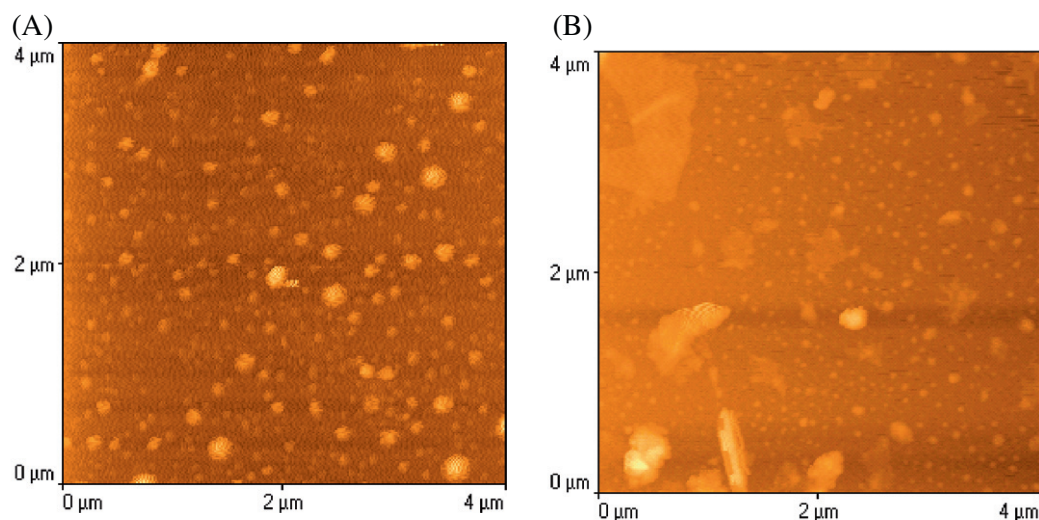

Fig. 10 – AFM images of the C_8SiGO particles obtained from (A) GO-L-5 and (B) GO-S-1 on a mica surface.

and 0.55 per GO unit. The sheet resistance was almost identical independent of the film thickness. This indicates that the amount of residual silica gives negligible effect on the resistance of carbon film.

4.   Conclusions

By using a chloroform/cyclohexane dispersion of silylated GO containing *n*-hexadecylamine, thin film samples were prepared by a cast method at a low temperature. Carbon films were successfully obtained from the pyrolysis of the resulting film under a reduced pressure at 500 °C or higher temperatures. The resistivity decreased with the increase in the film thickness or the decrease in the transparency. Based on the results obtained for the films prepared from GO samples with different particle sizes or oxygen contents, the conduction of the electrons within each carbon sheet seemed important for large film thickness and conduction through the boundary seemed important when the film thickness was small. A low sheet resistance of 3.7 kΩ/sq for 80% of transmittance was achieved, when GO with a lower oxygen content was prepared from graphite with smaller particle sizes and the silylated samples were heated at 500 °C. When the sample was heated at higher temperatures, the sheet resistance further decreased to a value of 0.7 kΩ/sq for 80% of transmittance of 900 °C.

Acknowledgment

R E F E R E N C E S

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